Short communication

A water management system for metal-based micro passive direct methanol fuel cells

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HIGHLIGHTS

- Aluminum alloy is used to fabricate cathode end plate with perforated flow filed.
- Water-collecting channels and PEO coating are fabricated on cathode end plate.
- Air-breathing holes can be free of water accumulation.
- Water flooding of cathode flow field can be prevented.

ARTICLE INFO

ABSTRACT

A novel water management system for micro passive DMFC is fabricated and characterized in this paper. This system consists of both a cathode current collector made of a 316L sintered stainless fiber felt (SSFF) and an aluminum-based end plate fabricated with a perforated flow field. Besides, some water-collecting channels were fabricated on the surface of the cathode end plate and then covered by the plasma electrolytic oxidation (PEO) coating. The results show that the PEO coating plays crucial roles in the water management system. Because of the highly hydrophilic property of the coating, the channels work well in collecting the liquid water from the current collector, and water accumulation along the air-breathing holes can be well prevented, which improves the stability of the micro DMFC.

1. Introduction

With the rapid development of portable electric devices, there has been an ever-increasing demand on micro power sources with high energy density. Direct methanol fuel cell (DMFC) is an attractive candidate due to its simple structure, instantly recharging and prospective energy density [1—3]. To make it more competitive, DMFC can be operated in a passive mode by eliminating auxiliary devices, relying on diffusion and natural convection to provide fuel and oxygen [4,5]. Such a passive design simplifies the cell structure greatly, but the poor transport makes its performance worse than those running in an active mode [4—6].

Water flooding is one of the key issues that can lower the output power and deteriorate the stability of a micro passive DMFC [4]. On the cathode, water that is generated by oxygen reduction reaction, along with that crosses from the anode, transports through the diffusion layer to the flow field [7]. Unlike those running in an active mode where air flow can take the water away, a passive DMFC mainly rely on gravitational force or wettability gradients to get the liquid water off [4]. Such an operation mode can easily result in accumulation of liquid water inside the diffusion layer, forming a so-called water flooding problem and constraining oxygen transportation [4—7]. Thus, it is quite necessary to optimize the cathode structure to enhance the water removal ability.

In recent years, researchers have developed some methods to release the water flooding problem of a micro passive DMFC [8—12]. Chen and Li adopted metallic porous materials as cathode current collector, and the liquid water can be removed at a faster rate as a result of the capillary action in the porous structure [8,9].

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Some effective strategies to enhance water removal are achieved on silicon-based micro passive DMFCs [10–12]. Yao et al. fabricated some alternative hydrophilic and hydrophobic holes on the cathode plate [10]. Liquid water can be driven passively into the hydrophilic holes, while the hydrophobic holes provide the oxygen diffusion path. Peng and Zhou fabricated some capillary channels with hydrophilic surface along the ribs of the air-breathing holes [11,12]. The water generated on the surface of cathode diffusion layer can be drawn into these channels by capillary force. Despite the effective removal of water droplets in the aforementioned designs, it is clear that these silicon-based fabrication methods are not suitable for a metallic substrate.

In this communication, we proposed a novel water management system for metal-based micro passive DMFC to reduce the water flooding problem effectively. The system includes a hydrophilic coating, some water-collecting channels and a stainless steel felt fiber. A micro passive DMFC was fabricated with the novel structure and tested by polarization and constant-current-density discharging.

2. Design and fabrication

Fig. 1a schematically shows the structure of the micro passive DMFC. A 316L stainless steel fiber felt with 0.25 mm in thickness was used as cathode current collector. Aluminum alloy LY12 was adopted to fabricate the cathode end plate that had a perforated flow field, as shown in Fig. 1b. At the back side contacting with the current collector, there are several water-collecting channels with 0.3 mm in width and 0.5 mm in depth in the active area between every two rows of the holes. At the front side, several water-collecting channels are also fabricated to go through the plate, connecting with the ones at the back side. To make the liquid water flow fluently in the channels, two additional lines of holes were fabricated respectively on the top and bottom of the flow field.

In the design, liquid water produced inside the porous current collector is expected to be drawn into the water-collecting channels and flow down automatically under the gravity. To achieve this purpose, a highly hydrophilic coating (shown schematically in Fig. 1b as a gray part) was fabricated on the surface of the cathode end plate by plasma electrolytic oxidation (PEO) technology [13,14]. The PEO treatment was carried out for about 30 min in a mixed solution of 10 g L^{-1} Na_2SiO_3 and 1 g L^{-1} NaH_2PO_2 by a homemade 5 kW AC power supply with the frequency of 1000 Hz. The as-prepared coating is composed of aluminum silicate and aluminum oxide and possesses a typical crater-like structure resulting from the breakdown [15].

A micro DMFC with the novel structure was fabricated. Commercial anode (Pt loading: ca. 2 mg cm^{-2}) and cathode (PtRu loading: ca. 4 mg cm^{-2}) gas diffusion electrodes, purchased from Johnson Matthey, Inc., were attached to a pretreated Nafion membrane with hot pressing at 135 °C and 10 MPa for 180 s. The as-prepared membrane electrode assembly (MEA) has an active area of 1 cm^2. The anode current collector with some parallel channels and 43.2% open ratio was fabricated with 316L stainless steel. To reduce the contact resistance, all the current collectors were coated with 200 nm Au layer. As references, another two micro DMFCs were also fabricated. One of them (named as reference-a cell for simple description) is a conventional one whose cathode current collector has perforated flow field and is coated with Au layer. The other (named as reference-b cell) has the same configuration as shown in Fig. 1a, but its cathode end plate is covered by Au layer instead of PEO coating. The Au deposition does not cause significant variation to the water management of reference-b cell because the wettability of the end plate does not change a lot with the Au layer [16].

In our micro DMFCs, air was supplied to the electrodes through the open areas only by diffusion, and methanol solution diffused into the anode catalyst layer from a 2.5 mL reservoir that was adhered to the anode fixture. Prior the performance test, the cell
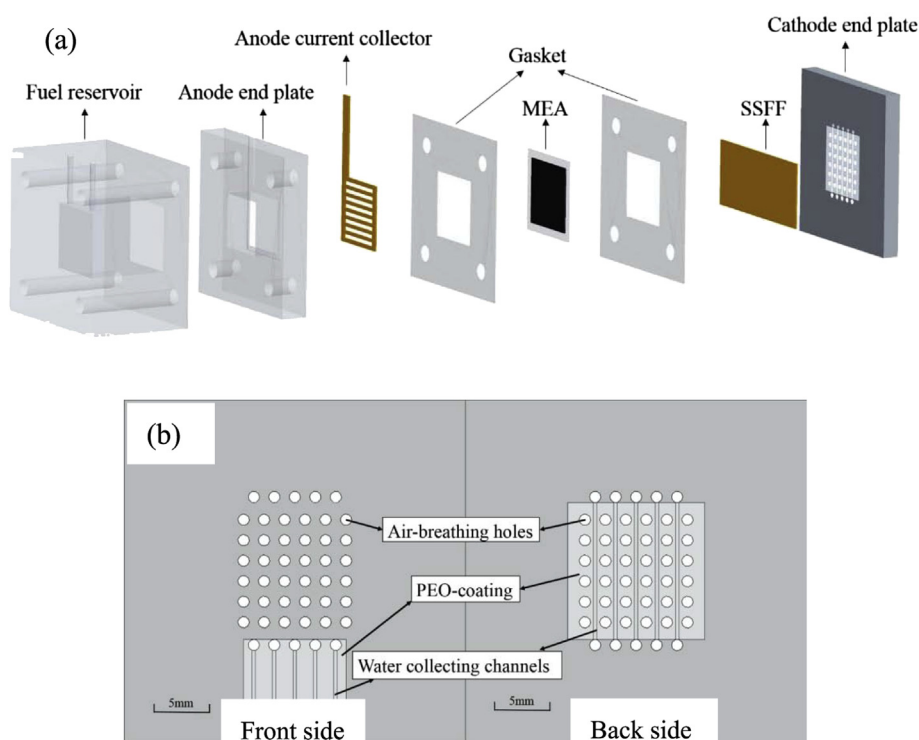

Fig. 1. Schematic structure of the novel micro passive direct methanol fuel cell (a) and the cathode end plate (b).

was activated with 2 M methanol solution, and then the current–voltage (*i*–*V*) and current-power (*i*–*P*) curves were obtained by gradually increasing the current at the interval of 10 mA. Per one step, the current holding time was 120 s.

3. Results and discussion

The PEO coating prepared in our experiment is highly hydrophilic, as shown in Fig. 2. When a water droplet of ca. 5 μl is dispensed on the coating surface, an initial wetting angle of 12.7° is obtained. And then the water droplet gets into the coating quickly, which makes the wetting angle decrease to ca. 3.1° after a contacting time of ca. 0.2 s. The results reveal that the PEO-treated cathode end plate can show excellent water management. When the liquid water formed inside the cathode gas diffusion layer contacts the coating, it will be absorbed quickly by the PEO coating and gets into the water-collecting channels. Consequently, the cathode flow field can be free of water accumulation along the air-breathing holes. With the cell going on discharging, more water will accumulate inside the channels, flowing along the channels under gravity, and finally, the water will travel through the holes at the bottom of the flow field to the channels at the front side of the end plate.

To illustrate the effects of the novel structure on cell performance, Fig. 3 shows the polarization curves of the three cells at the room temperature of ca. 303 K with different methanol concentrations. Reference-a cell achieves its maximum value of peak power density of 16 mW cm^{-2} at 3 M methanol concentration, and a further increase in methanol concentration decreases the output power owing to the enhanced methanol crossover. Both reference-b cell and the novel cell give the maximum peak power densities at 4 M methanol concentration. This is because that the adoption of sintered stainless steel fiber leads to an improved distribution of compression force, which lowers methanol crossover and enables the cell to be operated at a higher methanol concentration [9,17]. But the novel cell does not show obvious difference in performance when compared with reference-b cell.

To confirm the superiority of the novel cathode structure, the three cells were discharged under a constant current density of 120 mA cm^{-2} for 90 min, and the results are shown in Fig. 4. Both the output voltages of the two reference cells decline quickly with
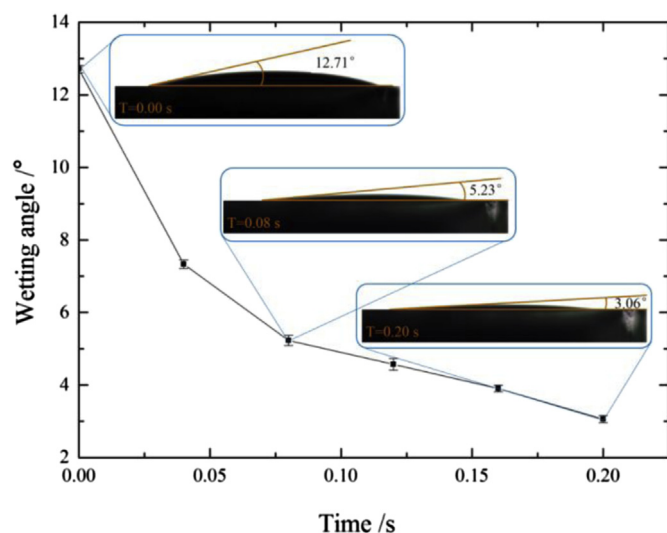

Fig. 2. Evolution of wetting angles when a water droplet (ca. 5 μl) was dispensed on the PEO coating.
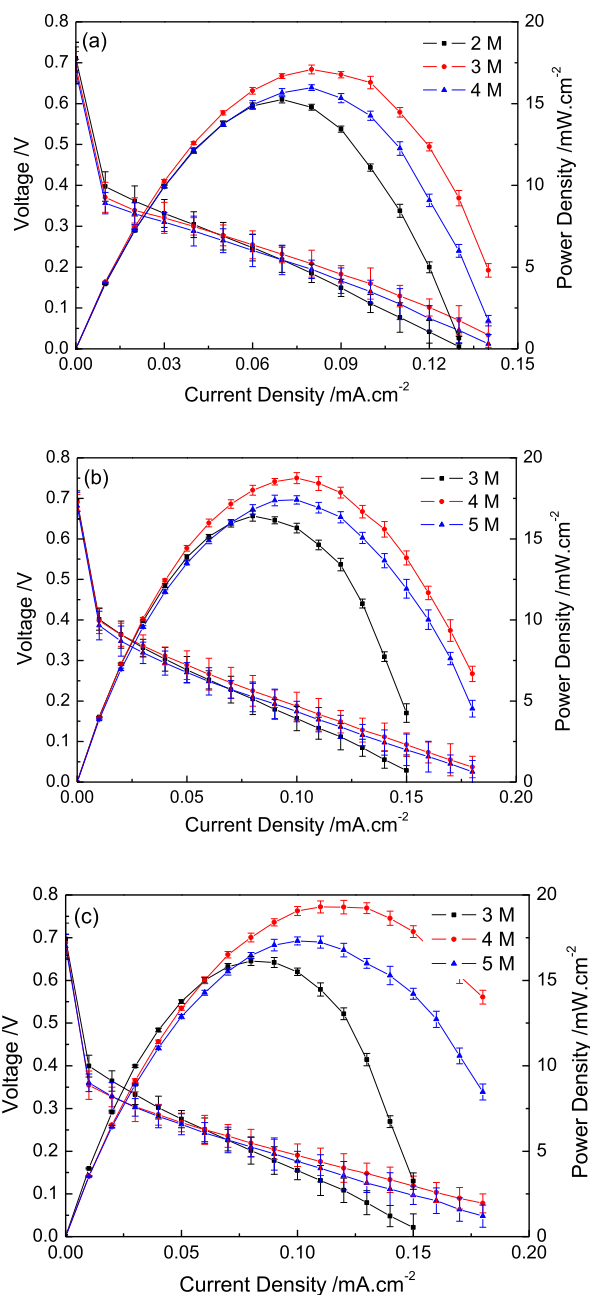

Fig. 3. Power density curves of reference-a cell (a), reference-b cell (b) and the novel cell (c) tested with different methanol concentrations under room temperature.

time, and reference-a cell and reference-b cell have their output voltages decrease from the initial values of 99.2 mV and 141.4 mV to the final values of 13.0 mV and 96.6 mV, respectively. The main reason behind the drop in voltage can be ascribed to methanol consumption or water flooding. To make this question clear, Table 1 lists the methanol concentrations before and after the constant-current-density discharging. For reference-a cell, the methanol concentration decreases from 9.87 wt.% to 7.28 wt.%. It can be found in Fig. 3 that reference-a cell can give an output voltage of ca. 60 mV when fed with 2 M (ca. 6.45%) and discharged at 120 mA cm^{-2}. This means that the final methanol concentration of reference-a cell is still high enough to support an output voltage much higher than that at the end of the discharging. In the same way, the final methanol concentration of reference-b cell is also able to support
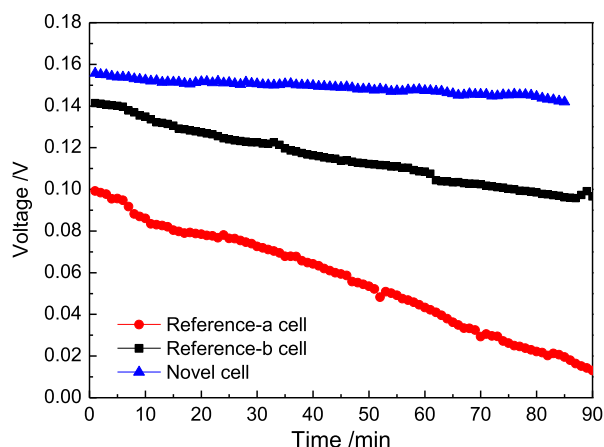
Fig. 4. Transient discharging curves tested under a constant current density of 120 mA cm^{-2} at room temperature.

Table 1
Methanol concentrations of reference-a cell, reference-b cell and the novel cell before and after discharging at 120 mA cm^{-2} for 90 min.

	Reference-a cell	Reference-a cell	Novel cell
Initial volume (ml)	2.00	2.00	2.00
Initial concentration (wt. %)	9.87	13.71	13.71
Final volume (ml)	1.78	1.81	1.80
Final concentration (wt. %)	7.58	12.33	12.41

an output voltage higher than that at the end of the discharging. This result shows that it is not methanol depletion but water flooding is the main cause that leads to the rapid drop of the output voltage during the discharging. As shown in Fig. 5a and b, many air-breathing holes of the two reference cells are filled with water droplets at the end of the discharging, which increases the oxygen transportation resistance to a great extent and thus deteriorates the output performance. Because of the fabrication of the micro channels, reference-b cell has its cathode flow filed experience less from water flooding than reference-a cell does, which results in better stability. But the water flooding problem of reference-b is still severe.

As for the novel cell, Fig. 4 reveals that its output voltage decreases very slowly with time. During the whole discharging process, the air-breathing holes of the novel cell almost keeps away from water flooding, as shown in Fig. 5c. After discharging for about 20 min, liquid water can be observed on the water-collecting channels fabricated on the front side of the cathode end plate, as shown in Fig. 5d. With the discharging going on, more liquid water is produced and flows along these channels, as shown in Fig. 5e. These results clearly indicate that the PEO coating plays crucial roles in the design of the water management system. Because of the hydrophilic property of the PEO coating, the liquid water formed inside the porous current collector is draw into the water-collecting channels fabricated on the back side of the cathode end plate, and then it flows along these channels under gravity to reach the channels on the front side of the cathode end plate. In this case, the cathode flow field and current collector are free of water flooding, which increases the discharging stability of the fabricated micro passive DMFC.

To gain an insight into how the electrode process is affected by the novel structure, an Ag/AgCl reference electrode is introduced to build a half-cell system inside the cell to measure the anode and cathode electrode potentials separately in situ [9], and the results are shown in Fig. 6. Since water flooding of the air-breathing holes does not occur, the novel cell has a stable cathode electrode potential. The anode electrode potential of the novel cell increases with time at a rate of ca. 0.07 mV min^{-1}, which indicates that methanol consumption leads to anode concentration loss and voltage decline. As for reference-b cell, its cathode electrode potential declines with time at a high rate of ca. 0.31 mV min^{-1} because the severe problem of water flooding enhances the oxygen
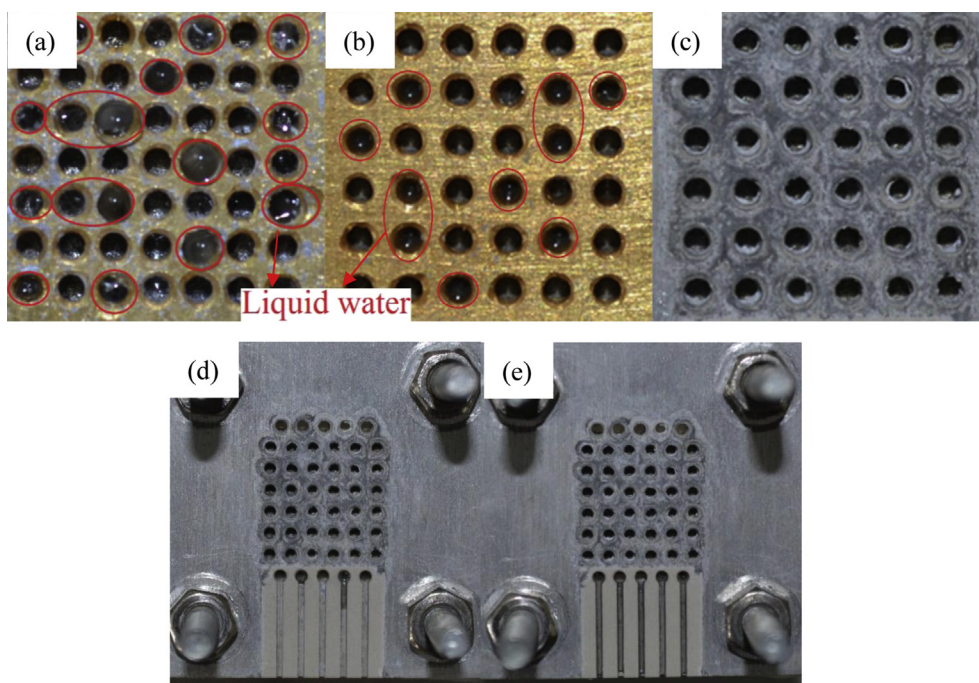

Fig. 5. Photographs of air-breathing holes of reference-a cell (a), reference-b cell (b) and the novel cell (c) after discharging for 90 min. Water flowing along the channels of the novel cell after discharging for 20 min (d) and 80 (e) min.
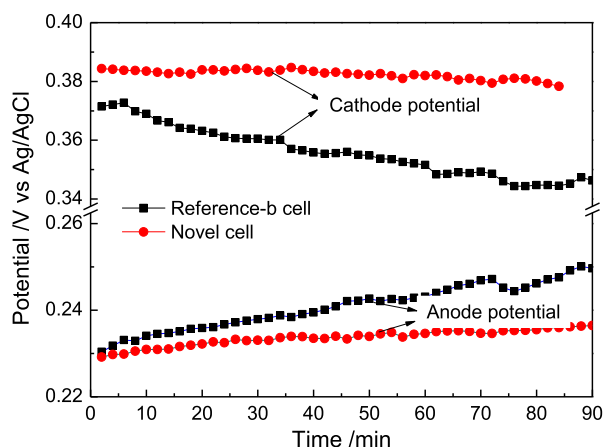
Fig. 6. Variation of the cathode and anode electrode potentials under the discharging current density of 120 mA cm^{-2}.

transportation resistance. The anode potential of reference-b cell increases with time at a higher rate (ca. 0.2 mV min^{-1}) than that of the novel cell does. The reason should be that much water accumulating at the cathode can increase the liquid water pressure or concentration inside the cathode catalyst layer and thus decrease the transport of water from anode to cathode. In this case, the anode catalyst layer of reference-b cell has a lower methanol concentration and a higher concentration polarization than that of the novel cell does. In summary, the results confirm that the PEO coating is an important part of the water management system of the novel cell.

4. Conclusions

An effective water management structure for metal-based micro passive DMFC was designed and tested. In this novel system, water-collecting channels, air-breathing holes and PEO coating were fabricated on the aluminum-based cathode end plate, and a stainless steel felt fiber was used as cathode current collector. Since the PEO coating is highly hydrophilic, liquid water can be taken into the PEO-treated water-collecting channels quickly when contacting the coating surface. In this case, water accumulation along the air-

breathing holes can be suppressed, and thus it prevents water flooding of the cathode flow filed, which improves significantly the performance and stability of the cell. By the holes connecting the channels on both sides of the cathode end plate, the water can transport from the inside to the outside, which provides the possibility to recycle the liquid water. Moreover, adopting stainless steel felt fiber as cathode current collector makes the cell operated at a higher methanol concentration.

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